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Generation of Nitrogen-Vacancy Center Pairs in Bulk Diamond by Molecular Nitrogen Implantation *

Zhao-Jun Gong(贡赵军), Xiang-Dong Chen(陈向东)**, Cong-Cong Li(李聪丛), Shen Li(李燊), Bo-Wen Zhao(赵博文), Fang-Wen Sun(孙方稳)

[1]*Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei 230026*
[2]*Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026*

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The coupled negatively charged nitrogen-vacancy (NV^-) center system is a promising candidate for scalable quantum information techniques. In this work, ionized nitrogen molecules are implanted into bulk diamond to generate coupled NV^- center pairs. The two-photon autocorrelation measurement and optically detected magnetic resonance measurement are carried out to confirm the production of the NV^- center pair. Also, both 1.3 μs decoherence time and 4.9 kHz magnetic coupling strength of the NV^- center pair are measured by controlling and detecting the spin states. Along with nanoscale manipulation and detection methods, such coupled NV^- centers through short distance dipole–dipole interaction would show high potential in scalable quantum information processes.

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Negatively charged nitrogen-vacancy (NV^-) centers in diamond with long decoherence time have been regarded as one of the most promising candidates for solid state quantum information techniques under ambient conditions.[1] The NV^- center consists of a substitutional nitrogen atom and an adjacent vacancy in the lattice. The overall negative charge is due to an additional captured electron, which makes the defect a bright single-photon emitter with zero phonon line at 637 nm.[2] The $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$ sublevels of the ground-state spin triplet (S=1) are separated by 2.87 GHz due to the spin–spin interaction.[3] Such an NV^- center can be found in natural diamond. However, the artificial fabrication[4] of NV^- centers with implantation of nitrogen ions makes it feasible in various applications. More importantly, the spin state of the NV^- center can be initialized, manipulated and read out with optics and microwaves.[5,6] These extraordinary properties make the NV^- center a huge potential in many fields such as quantum information processes,[7−9] single-spin magnetometry[10−13] and biology applications.[14,15]

Currently, numerous quantum information processes have been well demonstrated with single NV^- centers. However, it is necessary to couple different NV^- centers for scalable quantum information techniques. One approach is to use a medium, such as photonic or superconductor qubit. In experiment, photon–spin entanglement has been produced.[9] Then, spin–spin entanglement in remote NV^- centers[16] can be generated by detecting the photons from two photon–spin entangled states based on the entanglement-swapping processes. Based on the remote spin–spin entanglement, quantum teleportation[17] and loophole-free Bell inequality test at 1.3 km[18] have been well demonstrated. However, the successful probability of the quantum information process with photon–spin entanglement is low due to the ultra-low photon coupling and detection efficiency from the NV^- center. Although the coupled NV^- centers through a superconductor qubit have been proposed,[19,20] the experimental demonstration is still with difficulties.[21] There is another approach to obtain coupled NV^- centers through short distance dipole–dipole interaction. When the distance between two NV^- centers is less than 20 nm, there is strong magnetic dipole–dipole interaction which scales as the inverse cube of separation distance. Based on the magnetic dipole–dipole interaction, spin–spin entanglement[22,23] has been demonstrated. To experimentally study such a coupled system, imaging and manipulation of nearby NV^- centers with the nanoscale spatial resolution[24,25] has also been realized.

In the natural diamond, the NV^- centers distribute randomly and the content is so low that it is hardly measured. Therefore, the fabrication of NV^- center pairs and detection of the coupling strength

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**Corresponding author. Email: xdch@ustc.edu.cn

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between coupled NV^- centers are critically required. Normal implantation with nitrogen ions would produce randomly located NV^- centers and the distance between nearby NV^- centers is undeterminable.[26,27] It is difficult to find isolated coupled NV^- center pairs with nanoscale distance.[22,23] In this work, we created NV^- center pairs in a high purity single crystal diamond by implanting ionized nitrogen molecules. The probability to generate NV pairs with nitrogen molecules could be higher than that with nitrogen ion implantation. By controlling the dosage and energy of the ionized nitrogen molecules, the distance between NV^- centers can be at tens of nanometers and coupled NV^- centers can be produced. By controlling the spin state with microwaves, a magnetic coupling strength of one NV center pair was measured to be 4.9 kHz based on the double electron–electron resonance (DEER). Such a coupled NV^- center pair would be applied in the quantum entanglement and electromagnetic measurement[28] with high resolution.

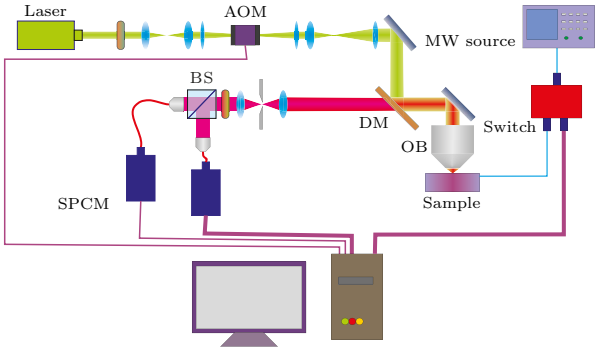

Fig. 1. The schematic drawing of the scanning confocal microscopy system for the control and detection of NV centers. The DM was used to reflect the pump laser at 532 nm and transmit the fluorescence photon from the NV center. The AOM was used to switch the exciting light on or off. On the sample, a 15-μm-diameter copper wire is placed to introduce the microwave from the microwave source. The laser and the microwave were controlled by a computer through AOM and switch.

In the creation process, a high-quality electronic grade CVD diamond sample (nitrogen concentration <5 ppb) provided by the Element 6 Company was used to generate NV^- center pairs by implanting nitrogen molecule ions with an IBBE device (maximum intensity: 15 mA, implantation energy: 30 keV, the ion dosage was 3×10^{11} cm^{-2}). Ionized nitrogen molecules instead of ionized nitrogen atoms was applied to obtain the close distance between NV^- centers with higher efficiency. The chemical bond of the nitrogen molecule was broken when it arrived at the surface of the bulk diamond during the implantation, and the two nitrogen atoms would split closer compared with the individual nitrogen ion implantation situation, which finally lead to a higher generation efficiency of NV^- center pairs with a nanoscale distance. Here we choose 30 keV implantation energy and the depth of implanted nitrogen ions was simulated by the method of stopping and range of ions in matter[29] to be at 40–60 nm under the surface of the bulk diamond. After the irradiation, the diamond sample was annealed under a high vacuum condition (10^{-6} Pa) for 2 h at 850℃ to mobilize the vacancies and generate NV^- centers. In the end, the diamond sample was boiled in a 1:1:1 mixture of sulfuric, nitric and perchloric acid at 250℃ for about 45 min to remove the non-diamond carbon admixtures.

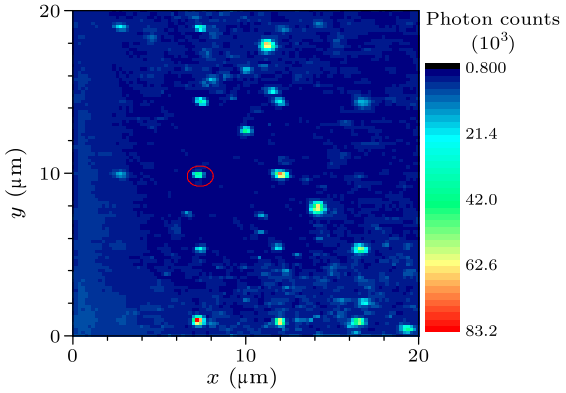

Fig. 2. The image of the NV centers in a 20×20 μm^2 area. The light spots were NV^- centers and the one marked by a red circle was the pair to be measured.

The diamond sample with NV^- centers was scanned with a home-built confocal microscopy system, as shown in Fig. 1. The sample was placed in a closed-loop piezoelectric transition stage (PZT) and excited by a 532 nm-wavelength continuous laser. An acoustic optical modulator (AOM) was used to switch the exciting light on or off. The fluorescent photons emitted from the NV^- centers were collected by a 0.9 N.A. objective lens and then transmitted through a dichroic mirror (DM) so that they could be coupled into a multi-mode fiber by a collimator. A 550 nm long-pass filter was used before the collimator to filter out the excitation light. The multi-mode fiber was connected to a single photon counting module (SPCM) to obtain fluorescence intensity (the signals from SPCM were counted by a counting board plugged in a personal computer). The scan process consisting of the PZT movement and the SPCM counting was controlled by a Labview program. Figure 2 shows the scanning fluorescence image of a 20×20 μm^2 area. The spot marked by the red circle is the NV^- center pair to be measured.

The result of two-photon autocorrelation measurement ($g^{(2)}(\tau)$) is illustrated in Fig. 3(a) with $g^{(2)}(0) = 0.41(2)$, which indicates two NV^- centers in the measurement area. The value of $g^{(2)}(0)$ is less than 0.5 due to the unbalanced fluorescent photon numbers from each NV^- center. The details of spin state resonant signals are obtained with the optically detected magnetic resonance (ODMR) measurement, as shown in

Fig. 3(b). The microwave is introduced to the NV$^-$ centers with a 15-μm-diameter copper wire. The NV$^-$ center has a triple spin ground state ($|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$) with $S = 1$. The splitting between these sublevels are changed in an external field. The nonresonant exciting laser can initialize the spin to $|m_s = 0\rangle$ through the spin-dependent intersystem crossing process.[30] Once the applied microwave is resonant, the NV$^-$ centers will be pumped from the initial state into the $|m_s = \pm 1\rangle$ state, which leads to a decrease in fluorescence intensity. During the ODMR measurement, we scanned the microwave frequency from 2.76 GHz to 2.88 GHz and recorded the variations of the fluorescence intensity. The two dips shown in Fig. 3(b) are at about 2.8072 GHz and 2.8292 GHz, representing the transition $|m_s = -1\rangle \leftrightarrow |m_s = 0\rangle$ from two different NV$^-$ centers under the magnetic field, respectively. The ODMR result also confirms that the marked spot in Fig. 2 is an NV$^-$ center pair.

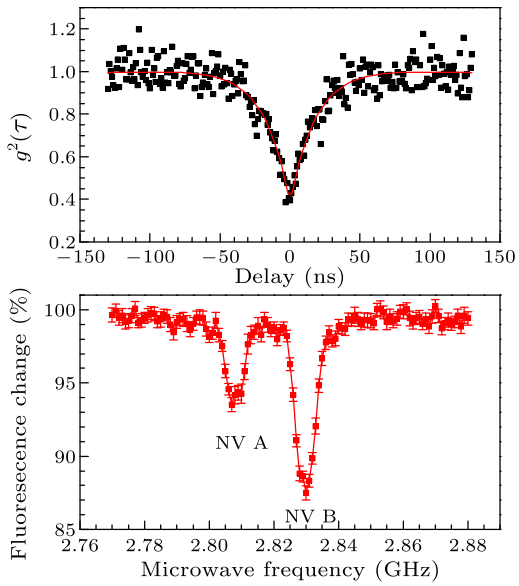

Fig. 3. (a) The two-photon autocorrelation measurement ($g^{(2)}(\tau)$). The value of $g^{(2)}(0)$ is less than 0.5 due to the unbalanced fluorescent photon number from each NV center. (b) The ODMR spectrum of the implanted two NV centers. Two dips at 2.8072 GHz (NV A) and 2.8292 GHz (NV B) represented two $|m_s = -1\rangle$ states from two different NV$^-$ centers.

After the ODMR measurement, the spin states of each NV can be separately controlled by different microwave pulses. The results of Rabi oscillation and Ramsey fringes of NV A are shown in Fig. 4. The Rabi oscillating period is about 260 ns. The decoherence time is estimated to be about $T_2^* \approx 1.3\,\mu$s from the Ramsey fringes, corresponding to the decoherence rate of 769 kHz. Therefore, to detect the weak dipole coupling, the dynamical-decoupling method should be applied. In the present sample, the probability to find such an NV$^-$ center pair for a long decoherence time is low. We have tested 173 pairs (points) and only the present pair can give meaningful data. Therefore, implantation parameters and the fabrication process need to be further improved to increase the yielding efficiency of long decoherence time NV$^-$ centers statistically.

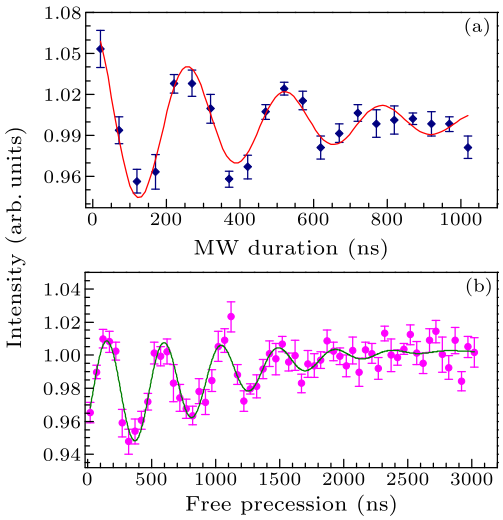

Fig. 4. Rabi oscillation (a) and Ramsey fringes (b) measurements of NV A on the spot. The Rabi oscillating period time is about 260 ns, and the decoherence time T_2^* is about 1.3 μs.

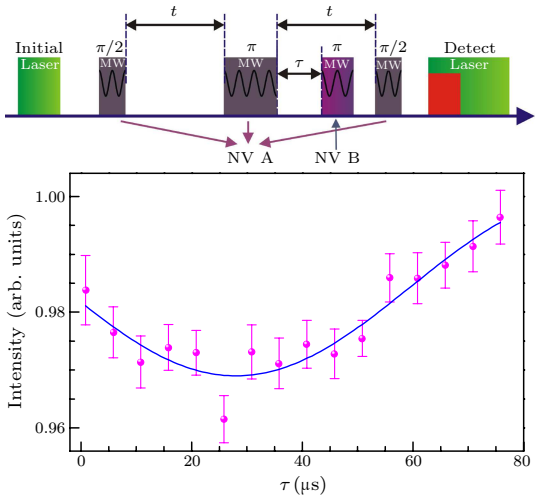

Fig. 5. The DEER technique applied to obtain a magnetic coupling strength of 4.9 kHz. The upper figure shows the pulse sequences for the measurements of coupling strength. Here t is set to be 76 μs, and the coupling strength is measured by changing τ.

To measure the coupling strength between two NV$^-$ centers in a pair, one of the NV$^-$ centers can act as a sensor and the other acts as an actuator. Here the DEER technique is applied to investigate the magnetic coupling between the pairs. If one electron spin in an NV$^-$ pair (spin A) is manipulated into a coherent superposition of its two eigenstates, the magnetic field created by the other spin in this pair (spin B) could induce the frequency in Ramsey interference

as $\omega_{\rm A}^{\rm Ramsey} = \omega_{\rm A}^{\rm Larmor} + \omega_{\rm A}^{\rm dip} \cdot m_{\rm S}^{\rm B}$, where $\omega_{\rm A}^{\rm Larmor}$ is the Larmor frequency of spin A, and $\omega_{\rm A}^{\rm dip}$ is the dipolar coupling frequency of the spin pair. With an external magnetic field, the different orientations of the two NV^- centers make it possible for the applied microwaves to address them independently. As shown in Fig. 5, the spin echo measurement was carried out on NV^- A in such a pulse sequence, while NV^- B was flipped after a τ time interval behind the π pulse on NV^- A, according to the DEER technique. The periodic modulation varies with τ and the dipolar coupling frequency of 4.9 kHz is obtained, corresponding to the magnetic coupling strength in the NV^--center pair.

Due to the relatively long distance between the two spins in this NV^- center pair, the coupling strength (4.9 kHz) is much less than the decoherence rate (769 kHz), which is not strong enough to obtain a stable entangled spin state in the NV^- center pair. To obtain a strong coupling strength, the implantation process could be more accurate in spatial resolution by controlling the energy of the ionized nitrogen molecules. Low energy might decrease the distance between NV^- centers. However, the NV^- pair yielding efficiency would drop. Moreover, the sample could be masked by lithography to obtain a more accurate spatial resolution during the implantation process so that the dipolar magnetic coupling strength could be enhanced. On the other hand, the diamond sample with isotopically enriched ^{12}C atoms can be used to obtain a long decoherence time for NV^- centers.[31] In the implantation process, the dosage of ionized nitrogen molecules should be decreased for keeping a relatively pure environment around artificial NV^- center pairs to control the deleterious decoherence. The co-implantation with ionized carbon atoms would be used for improving the coherence time of NV^- center pairs. An appropriate annealing process with different temperatures can also extend the decoherence time.[32,33]

In summary, we have created NV^- center pairs to reveal detective magnetic dipolar coupling in high purity bulk diamond by ionized nitrogen molecule implantation. The two-photon autocorrelation measurement and ODMR measurement are carried out to confirm the production of the NV^- center pair. The Rabi oscillations are achieved in the artificial NV^- center pairs. A magnetic coupling strength of 4.9 kHz is also obtained by applying the DEER technique. With the optimized implantation process, the decoherence time and magnetic coupling strength could be improved in the future, which will make it more realistic for quantum operation in solid-state qubits. As the ion implantation process could be integrated with nanoscale lithography, the implanted NV^- center pairs in particular positions of designed micro-nano structures on chip could also be realized. Furthermore, since the spin state in the coupled NV^- centers can be manipulated with the nanoscale charge state depletion nanoscopy[25] and measured with the quantum statistical image method,[24] such coupled NV^- centers through short distance dipole–dipole interaction show high potential in scalable quantum information techniques.

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